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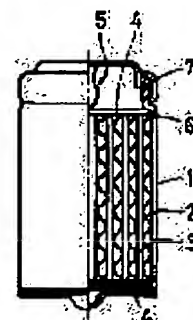
## (54) SECONDARY BATTERY

(57)Abstract:

PURPOSE: To secure safety while keeping excellent characteristics by keeping the moisture content in a nonaqueous electrolyte cell, in which an Li containing composite alloy oxide is used as a positive electrode active substance and a carbonaceous material as a negative electrode active substance, within a predetermined range.

CONSTITUTION: The battery comprises a positive electrode 1 in which a lithium containing composite alloy oxide is used as a positive electrode active substance, a negative electrode 3 in which a carbonaceous material is used as a negative electrode active substance, a separator 2, an organic electrolyte, and a cell housing.

The moisture content contained in the organic electrolyte is designed to be from 5 to 450ppm. When it exceeds 450ppm, hydrogen gas or the like is unfavorably generated upon an initial charging so that the internal pressure rises and the swelling in the cell takes place. On the other hand, controlling it below 5ppm unfavorably requires an extremely long time of dehydrating process and an extremely high-grade water content control in assembly man- hours. Accordingly, controlling it



within the range of 15-300ppm can maintain practical and excellent battery characteristics.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The rechargeable battery characterized by being the rechargeable battery which makes a basic component the positive electrode which makes a lithium content compound metallic oxide a positive active material, the negative electrode which makes carbonaceous material a negative-electrode active material, a separator, the organic electrolytic solution, and a cell container, and the moisture content contained in this organic electrolytic solution being 5 ppm - 450 ppm.

[Claim 2] The rechargeable battery according to claim 1 characterized by coming to prepare one [ at least ] electrode an active material coat on a metal charge collector, and distributing the binder in this active material coat by the binder distribution factors 0.5-5.0.

[Claim 3] The rechargeable battery according to claim 2 characterized by for a metal charge collector being a metallic foil, and the surface roughness of this metallic foil being 0.1 micrometers - 0.9 micrometers.

[Claim 4] The rechargeable battery according to claim 2 characterized by making into a principal component the styrene / butadiene latex a binder is 40 % of the weight - 95 % of the weight of butadiene contents, and is [ latex ] 75% - 100% of gel contents.

[Claim 5] The rechargeable battery according to claim 1 characterized by the thing for which the organic electrolytic solution was chosen from ether, ketones, lactone, nitril, amines, amides, a sulfur compound, chlorinated hydrocarbons, ester, carbonate, the nitro compound, the phosphoric ester system compound, and the sulfolane system compound, and which use a kind as a solvent at least.

[Claim 6] The rechargeable battery according to claim 1 characterized by this negative electrode occupying both the most inner circumference and the outermost periphery in the cell structure which carries out separator \*\* of the positive/negative electrode, and carries out opposite arrangement and it comes to involve in.

[Claim 7] The rechargeable battery according to claim 1 characterized by equipping with the PTC element whose induction temperature coefficient operation temperature is 80 degrees C - 140 degrees C, and is -10--130 as a safety device.

[Claim 8] Operation of the rechargeable battery characterized by making the pocket electronic equipment which consists of IC elements which operate by 3.5V-2.6V drive in the rechargeable battery single cell whose moisture content contained in this organic electrolytic solution it is the rechargeable battery which makes a basic component the positive electrode which makes a lithium content compound metallic oxide a positive active material, the negative electrode which makes carbonaceous material a negative-electrode active material, a separator, the organic electrolytic solution, and a cell container, and is 5 ppm - 450 ppm.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the new rechargeable battery excellent in cycle nature, a preservation property, and safety.

[0002]

[Description of the Prior Art] In recent years, various non-drainage system rechargeable batteries are proposed as small and the lightweight rechargeable battery which change to the conventional acid-lead cell, and nickel/cadmium cell. The new rechargeable battery system which uses carbonaceous material for a negative electrode especially using the compound metallic oxide which makes Li and Co a principal component in the positive electrode currently indicated, for example in JP,62-90,863,A, JP,63-121,260,A, JP,3-49,155,A, etc. attracts attention.

[0003] What uses Metal Li or Li alloy was conventionally proposed as a negative-electrode active material as this non-drainage system rechargeable battery. From small and a viewpoint of being lightweight, although the rechargeable battery which used this metal Li etc. for the negative electrode was satisfied, it had the serious obstacle to utilization, such as performance problems, such as cycle nature, a preservation property, etc. based on a dendrite deposit, and a problem of the life of the separator by dendrite deposit breaking through similarly and causing the interior short circuit of a shell, and a problem when [ safe ] based on still activity Metal [ Li ] chemical reactivity.

[0004] On the other hand, since the new fuel cell subsystem which uses carbonaceous material for the aforementioned negative-electrode active material does not have activity chemical reactivity like Metal Li while having the outstanding cycle nature and the outstanding preservation property, without causing such a dendrite deposit, it has the feature that safety is very excellent.

[0005] When it combines with Li content compound metallic oxide as a positive active material especially, it is expected as what can do the cell of the high voltage and high capacity.

[0006]

[Problem(s) to be Solved by the Invention] By the way, this Li content compound metallic oxide is made into a positive active material, and the performance of a cell and safety are greatly influenced by the moisture content contained in the electrolytic solution to be used in the nonaqueous electrolyte cell using carbonaceous material as a negative-electrode active material. For example, when many moisture contains in the electrolytic solution in remainder, while the bad influence on performances, such as decline in current efficiency and a fall of cycle nature, comes out, the phenomenon which becomes safe upper problems, such as the generation of gas and internal pressure elevation, by the reaction with moisture occurs.

[0007] However, although it is theoretically possible to make the moisture content in the electrolytic solution about into zero when the manufacturing process of an actual cell is considered, it becomes high in cost extremely. When using especially the carbonaceous material of this invention for a negative-electrode active material, the moisture content permitted differs from the case where the conventional metal Li is used as a negative-electrode active material. Therefore, it is an important technical problem to clarify the moisture content permitted in the fuel cell subsystem of this invention, and to find out the balance range of practicality.

[0008]

[Means for Solving the Problem and its Function] As a result of considering wholeheartedly the influence by the moisture content of this fuel cell subsystem, this invention person etc. maintained the property which was excellent in the specific moisture-content range, and found out that safety was also secured.

[0009] The rechargeable battery of this invention is a rechargeable battery which makes a basic component the positive electrode which was completed based on this knowledge and makes a lithium content compound metallic oxide a positive active material, the negative electrode which makes carbonaceous material a negative-electrode active material, a separator, the organic electrolytic solution, and a cell container, and is characterized by the moisture content contained in this organic electrolytic solution being 5 ppm - 450 ppm.

[0010] In this invention, especially the content moisture content must be important and the range of it must be 5 ppm - 450 ppm. It is the range of 15 ppm - 300 ppm preferably.

[0011] In exceeding 450 ppm, while gas, such as hydrogen gas, occurs at the time of initial charge and internal pressure rises, phenomena, such as blistering of a cell, generate and are not desirable. Moreover, in order to control to a less than 5 ppm moisture content, while very prolonged dehydration processing is required like the above-mentioned, it is not set like an erector and moisture needed [ very advanced ], and desirable.

[0012] In order to control a moisture content in the range of this invention, about the electrolytic solution, the method of using dehydrating agents, such as molecular sieves, etc. is adopted. moreover, members, such as positive, a negative electrode, and a separator, -- about moisture, each may be dried preparatorily and methods, such as establishing a dryness process before electrolytic-solution sinking in like a cell erector, are adopted

[0013] Moreover, since the activity matter is not used for positive [ of the combination of this invention ], and the negative electrode to the moisture of a metal lithium etc., especially advanced dry conditions are not so required for them as the erector. When establishing a dryness process especially before electrolytic-solution sinking in, even if it performs the process till then in the usual atmosphere, it can be controlled to the moisture content of the limited range of this invention.

[0014] Like the above, in the case of the cell of positive [ of this invention ], and the combination of a negative electrode, the moisture content of the latus range is permitted compared with the conventional lithium cell etc., and it becomes a practically big advantage.

[0015] Li compound metallic oxide as used in the field of this invention is a compound which has the layer structure, and Li ion intercalates and can deintercalate electrochemically.  $\text{LiCoO}_2$  which will be indicated, for example by JP,55-136,131,A if an example of this compound metallic oxide is shown, although not limited especially, and the general formula  $\text{Li}_x \text{Co}_y \text{N}_z \text{O}_2$  (however) currently indicated by JP,62-90,863,A N was chosen from the group of aluminum, In, and Sn -- a kind is expressed at least and x, and y and z express the number of each  $0.05 \leq x \leq 1.10$ ,  $0.85 \leq y \leq 1.00$ , and  $0.001 \leq z \leq 0.10$   $\text{Li}_x \text{Ni}_y \text{Co}_{(1-y)} \text{O}_2$  [ moreover, ] (however,  $0 < x \leq 1$ ,  $0 \leq y < 0.50$ ) indicated by JP,3-49,155,A -- further --  $\text{Li}_x \text{MnO}_2$  etc. -- it is mentioned

[0016] In order to obtain this compound, if it requires further, it will be easily obtained by the baking reaction with other metallic compounds with Li compounds, such as a lithium hydroxide, a lithium oxide, a lithium carbonate, and a lithium nitrate, a metallic oxide and a metal hydroxide, a metal carbonate, a metal nitrate, etc.

[0017] Each of these multiple oxides has the outstanding property which is not seen in other active materials called the high voltage and high capacity as a positive active material. especially the aforementioned general formula  $\text{Li}_x \text{Co}_y \text{N}_z \text{O}_2$  (however, N was chosen from the group of aluminum, In, and Sn -- expressing a kind at least, x, and y and z express the number of each  $0.05 \leq x \leq 1.10$ ,  $0.85 \leq y \leq 1.00$ , and  $0.001 \leq z \leq 0.10$ ) especially is a multiple oxide which is excellent in properties, such as cycle nature, and is preferably used by this invention

[0018] Moreover, although especially the carbonaceous material as used in the field of this invention is not limited, if it shows the example, baking carbide, such as a high surface-area carbon material given in JP,58-35,881,A, graphite, and a phenol system resin given in JP,58-209,864,A, the baking carbide of a condensation polycyclic hydrocarbon system compound given in JP,61-111,907,A, etc. will be mentioned. The carbonaceous material which has the BET adsorption method specific surface area A ( $\text{m}^2 / \text{g}$ ) indicated by JP,62-90,863,A especially in the range in which the value of the crystal thickness Lc in an X diffraction (A) and true density  $\rho$  ( $\text{g}/\text{cm}^3$ ) fills the following conditions  $1.70 < \rho < 2.18$  and  $10 < Lc < 120\rho - 189$  in  $0.1 < A < 100$  has high capacity and the outstanding cycle property, and is especially used preferably in this invention.

[0019] Although it is not limited, after especially the forming method of the electrode using this active material distributes an electrode active material in the solvent solution of an organic polymer, the coating method which carries out coating dryness can attain a thin film and large area-ization, and it is desirable. [ of a method ] In this case, that come to prepare one [ at least ] electrode an active material coat on a metal charge collector, and the binder in this active material coat is distributed by the binder distribution factors 0.5-5.0 prevents the fall of paint film intensity, the poor contact between active material particles, etc., it can improve the elevated-temperature property of the rechargeable battery of this invention, and it is desirable. a binder distribution factor -- desirable -- 0.75-2.5 -- it is 0.75-2.0 more preferably

[0020] The binder distribution factor said here is a coefficient defined by the below-mentioned measuring method, and the ratio of the amount of binders which exists in 10-micrometer layer thickness from an active material layer front face, and the amount of binders which exists in 10-micrometer layer thickness from a charge collector side active material layer interface is expressed.

[0021] <measurement of a binder distribution factor> -- sample: -- an electrode is hardened by the epoxy resin and let what carried out cutting polish of the electrode cross section be a sample

[0022] Measurement: Measure the amount of binders in the active material of an electrode cross section by EPMA

(electron microprobe analysis method).

[0023] Equipment is HITACHI. X-650 (Hitachi make)

HORIBA EMAX-2200 (Horiba make)

Wavelength-dispersion type EPMA is used.

[0024] <Calculation of a binder distribution factor> A lower formula performs a binder distribution factor.

[0025]

[Equation 1]

$$\text{バインダー分布係数} = \frac{\text{活物質層表面から } 10 \mu \text{ までの層のバインダー量}}{\text{集電体側活物質界面から } 10 \mu \text{ までの層のバインダー量}}$$

In addition, pretreatment of dyeing for the above-mentioned measurement etc. is arbitrarily chosen according to the kind of binder.

[0026] When the distribution factor of a binder is less than 0.5, the intensity on the front face of a paint film is weak, and lack of an active material etc. generates and is not desirable. Moreover, when a binder distribution factor exceeds 5.0, cell performances, such as a cell property especially cycle nature, a preservation property, and output characteristics, get worse and are not desirable.

[0027] In order to set a binder distribution factor to 0.5-5.0, it is attained by optimizing the conditioning in the describing [ above ] coating method. As a condition factor at that time, selection of a binder, selection of a coating liquid solvent, coating liquid viscosity, coating liquid solid concentration, the dryness method, drying temperature, etc. are mentioned.

[0028] Although not limited especially, generally the direction [ a rate of drying is slow ] gives a result with the higher one desirable [ coating liquid viscosity and solid-content concentration ].

[0029] Although not limited especially as a metal charge collector used for an electrode, since that a metal charge collector is a metallic foil, and the surface roughness of this metallic foil is 0.1 micrometers - 0.9 micrometers strengthens the adhesive property of an active material and a metallic foil and it can improve an elevated-temperature property too, it is desirable.

[0030] The appearance of this metallic foil presents grinding. 0.2-0.8-micrometer 0.1-0.9 micrometers are preferably controlled by etching processing, the lasing, electroless deposition, electrolysis plating, sandblasting, etc. still more preferably as surface roughness to the aforementioned metallic foil which has the appearance of gloss and semigloss at 0.6-0.8 micrometers. Moreover, you may use what goes into the above-mentioned surface roughness range among the copper foil directly obtained by electrolysis plating, a nickel foil, etc.

[0031] Hardly, if there is no adhesive improvement and 0.9 micrometers is exceeded, it causes cutting of a metallic foil into coating and is desirable at less than 0.1 micrometers of surface roughness.

[0032] 30-300 micrometers of thickness of the positive active material and binder which have been pasted up on the metallic foil are 70-130 micrometers more preferably per one side. As a metallic foil used for a positive electrode, aluminum with a thickness of 100-5 micrometers, nickel, a stainless steel, etc. can be used. It is aluminum preferably and a 30-10-micrometer thing is used still more preferably the thickness of 50-8 micrometers.

[0033] Moreover, 60-750 micrometers of thickness of the negative-electrode active material and binder which have been pasted up on the metallic foil are 140-400 micrometers more preferably per one side. As a metallic foil used for a negative electrode, copper with a thickness of 100-5 micrometers, nickel, a stainless steel, etc. can be used. It is copper and a stainless steel preferably and a 25-8-micrometer thing is used still more preferably the thickness of 50-6 micrometers.

[0034] Manufacture of the test piece for measuring surface roughness is first started on 1cm square from a metallic foil, puts this into a mold, and slushes and stiffens an epoxy resin. In ordinary temperature, it takes out from a mold, and cuts after neglect between days, the resin cutting plane containing a metallic foil is ground with the grinder which rotates and revolves around the sun, and the microphotography of a cross section is taken after an air blow. The depth of the crevice on the front face of a metallic foil is measured with an enlargement, and let the average depth be surface roughness.

[0035] The adhesive test of an active material particle and a metallic foil is cut out by width of face of 2cm to a metallic foil from an application or the electrode by which sizing was carried out by carrying out coating, drying and carrying out a compression press, and cuts out an active material particle and a binder by NT cutter in length of 5cm. Let this be a test sample.

[0036] The 2cm portion is exfoliated from the edge in the length direction of the piece of decision in the active material and binder which were pasted up, a metallic foil front face is taken out, and this portion is stopped and hung with a

stapler to a metal plate.

[0037] Next, methanol 80ml is put into a 100ml glass beaker. The above-mentioned glass beaker is put into an ultrasonic washer [a model (Yamato 2200)], and tap water is added between a scrubber container and a glass beaker, and it is made for the water surface to come upwards for a while from a methanol oil level.

[0038] The aforementioned test sample is made to sink in completely [ 3cm of active material particle jointing ] in a methanol, and a metal plate is hung with thread. The start button of an ultrasonic washer is pushed, an ultrasonic wave is generated, and a paint film front face is observed. It observes whether with time progress, a blister is produced from a start on an adhesion surface.

[0039] Especially as a binder which makes an active material bind to a charge collector, although not limited, various organic polymers are usually used. If an example of this binder is shown, the poly fluoride vinyl, a polyvinylidene fluoride, a fluororubber, a polyacrylonitrile, polymeter RIRONI tolyl, a nitrile rubber, ethylene-propylene rubber, a styrene butadiene rubber, a polymethylmethacrylate, a polysulfide rubber, a cyanoethyl cellulose, a methyl cellulose, etc. will be mentioned.

[0040] It faces using this organic polymer as a binder, and the method using the thing which made the binder solution made to dissolve this organic polymer in a solvent distribute an electrode active material as coating liquid, the method using the thing which made the water emulsification dispersion liquid of this organic polymer distribute an electrode active material as coating liquid, the method of applying the solution and/or dispersion liquid of this organic polymer to the electrode active material by which preforming was carried out beforehand, etc. are mentioned as an example.

[0041] although especially the amount of binders to be used is not what is limited -- usually -- the electrode active material 100 weight section -- receiving -- 0.1 - 20 weight section -- it is the range of 0.5 - 10 weight section preferably

[0042] Making into a principal component the styrene / butadiene latex a binder is 40 % of the weight - 95 % of the weight of butadiene contents, and is [ latex ] 75% - 100% of gel contents especially can improve an elevated-temperature property, and it is desirable.

[0043] The gel content of the polymer which a butadiene content is 40 % of the weight - 95 % of the weight, makes dry this styrene / butadiene latex further by manufacturing this styrene / butadiene latex industrially by the usual emulsion-polymerization method, and is obtained is 90% - 100% preferably 75% to 100%. Here, a gel content means the insoluble matter of the polymer to toluene.

[0044] When a butadiene content is less than 40 % of the weight, the bond strength and flexibility of an electrode are missing. Moreover, a bond strength is missing when it exceeds 95 % of the weight.

[0045] When a gel content is less than 75%, while the bloating tendency-proof to the electrolytic solution used for the bond strength and the non-drainage system cell mentioned later of an electrode is missing, the charge shelf-life ability under a high temperature service falls.

[0046] Although it is not certain why the gel content of styrene / butadiene latex polymer affects elevated-temperature shelf-life ability, it is imagined as that to which the polymer which it is affected, the bridge formation degree, i.e., the gel content, of latex polymer, and cannot carry out a flow to the flow of the polymer under an elevated temperature easily suppresses the fall of the service capacity after elevated-temperature preservation.

[0047] Moreover, the monomer in which the copolymerization of those other than styrene and a butadiene is possible can be used for styrene / butadiene latex, for example, ethylene nature unsaturated carboxylic acids, such as an acrylic acid, a methacrylic acid, an itaconic acid, a fumaric acid, and a maleic acid, can be used for ethylene nature unsaturation carboxylates, such as methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta) acrylate, acrylonitrile (meta), and hydroxyethyl (meta) acrylate, and a pan. It is desirable to use dicarboxylic acids, such as an itaconic acid, a fumaric acid, and a maleic acid, especially as an ethylene nature unsaturated carboxylic acid in respect of the bond strength of an electrode. Common practice, such as adjustment of polymerization temperature, adjustment of the amount of polymerization initiators, and adjustment of the amount of chain transfer agents, is used for adjustment of a gel content.

[0048] Although it does not limit especially, 0.01-0.5 micrometers of particle diameters of this styrene / butadiene latex are 0.01-0.3 micrometers more preferably.

[0049] although especially the loadings of this latex are not what is limited -- usually -- the active material 100 weight section -- receiving -- 0.1 - 20 weight section -- it is 0.5 - 10 weight section preferably

[0050] Adhesive strength good in under the 0.1 weight section is not obtained, but if 20 weight sections are exceeded, an overvoltage will go up remarkably, and it is \*\*\*\*\* about a bad influence to a cell property.

[0051] Moreover, although especially the solid-content concentration of coating liquid is not limited, it is usually 40 % of the weight - 65 % of the weight preferably 30 % of the weight to 65% of the weight.

[0052] Furthermore, \*\*\*\* for 2 - 60 weight sections is also good to styrene / butadiene latex solid-content 100 weight section in a water-soluble thickener as an additive.

[0053] As a water-soluble thickener, a carboxymethyl cellulose, a methyl cellulose, a hydroxymethyl cellulose, an ethyl



cellulose, polyvinyl alcohol, a polyacrylic acid (salt), oxidization starch, phosphorization starch, casein, etc. are contained.

[0054] Moreover, any components other than a water-soluble thickener are not eliminated an active material, styrene / butadiene latex, and if needed. For example, dispersants, such as sodium hexametaphosphate, the Tripoli sodium phosphate, pyrophosphoric-acid soda, and a sodium polyacrylate, and the thing which added additives, such as Nonion nature as a stabilizing agent of a latex and an anionic surfactant, further are also contained. the mean particle diameter of the carbonaceous material which is a negative-electrode active material when using styrene / butadiene latex -- decline in current efficiency, and the fall of the stability of a slurry -- \*\*\*\* -- having -- it is preferably more suitable than problems, such as increase of the resistance between particles within the paint film of an electrode, that it is [ 0.1-50-micrometer / 3-25-micrometer ] the range of 5-15 micrometers still more preferably

[0055] Application dryness of the slurry is carried out on a base material as coating liquid, and an electrode is fabricated. If it requires at this time, you may fabricate with charge collector material, and charge collectors, such as aluminum foil and copper foil, can also be used as a base material as an exception method.

[0056] Moreover, as this method of application, arbitrary coater heads, such as the reverse rolling method, the comma bar method, the GURABIYA method, and the air knife method, can be used.

[0057] Although are not limited especially as a separator, and textile fabrics, a nonwoven fabric, a glass cloth, a synthetic-resin fine porous membrane, etc. are mentioned, when using a thin film and a large area electrode, the synthetic-resin fine porous membrane indicated by JP,58-59072,A, especially a polyolefine system fine porous membrane are desirable in respect of thickness, intensity, and a membrane resistance.

[0058] Although not limited especially as an electrolyte of nonaqueous electrolyte, if an example is shown  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ , and  $\text{CF}_3\text{SO}_3\text{Li}$ , 2  $(\text{CF}_3\text{SO}_2)\text{N-Li}$ ,  $\text{LiPF}_6$ ,  $\text{LiI}$ ,  $\text{LiAlCl}_4$ ,  $\text{NaClO}_4$ ,  $\text{NaBF}_4$ ,  $\text{NaI}$ , 4  $(\text{n-Bu})\text{N}^+\text{ClO}_4$ , 4  $(\text{n-Bu})\text{N}^+\text{BF}_4$ , and  $\text{KPF}_6$  etc. -- it is mentioned

[0059] As an organic solvent of the electrolytic solution used, although ether, ketones, lactone, nitril, amines, amides, a sulfur compound, chlorinated hydrocarbons, ester, carbonate, a nitro compound, a phosphoric ester system compound, a sulfolane system compound, etc. can be used, for example, ether, ketones, nitril, chlorinated hydrocarbons, carbonate, and a sulfolane system compound are desirable also among these. Furthermore, it is annular carbonate preferably. As these examples of representation, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 4-dioxane, an anisole, a monochrome glyme, an acetonitrile, A propionitrile, a 4-methyl-2-pentanone, a butyronitrile, Valeronitrile, a benzonitrile, 1, 2-dichloroethane, gamma-butyrolactone, Dimethoxyethane, a methyl fall mate, propylene carbonate, Although ethylene carbonate, vinylene carbonate, a dimethylformamide, dimethyl sulfoxide, a dimethyl thio formamide, a sulfolane, a 3-methyl-sulfolane, trimethyl phosphate, phosphoric-acid triethyl, these mixed solvents, etc. can be raised It is not necessarily limited to these.

[0060] Furthermore, if it requires, a cell is constituted using parts, such as a charge collector, a terminal, and an electric insulating plate.

[0061] Although the gestalt of the cylinder-like cell around which it is not limited and a positive electrode, a negative electrode, the paper type cell that used the separator as the monolayer or the double layer, the laminating type cell or the positive electrode, the negative electrode, and the separator were wound in the shape of a roll especially as structure of a cell is mentioned as an example If it is the cell structure where carry out separator \*\* of the positive/negative electrode, carry out opposite arrangement, come to involve in, and a negative electrode occupies both the most inner circumference and the outermost periphery, since the amount of the metal lithium which deposits can be decreased remarkably Degradation by the fall of the cell capacity by repeat use, self-discharge, and the surcharge can be prevented, and it is desirable.

[0062] In this structure, it is the point for the section and the end section of a volume to wear a positive-active-material side completely by the negative electrode through a separator at electrode volume the beginning of a winding object, and to make it not exposed [ a positive active material ]. Although the negative electrode used at this time made only one side of a metallic foil charge collector install an active material, even if what doubles a metallic foil side and becomes in piles may be used for it and the thing which made both sides of a metallic foil install an active material uniformly is used for it, it is not cared about. Also in a positive electrode, it is the same.

[0063] Although the shorter one is good when the length with a negative electrode excessive seen from a positive electrode considers the amount of stuffing for a positive-active-material side a wrap case completely by the negative electrode through a separator, when a too short design is carried out, there is a possibility that the winding object which a positive active material exposes may be made according to factors, such as thickness dispersion of each electrode and electrode length measurement precision of take-up motion. Therefore, the distance between each edge of positive [ which it \*\*\*\*, and a positive electrode is completely covered by the negative electrode through a separator in a portion and the end portion of a volume, and counters through a separator in the aforementioned part ], and a negative electrode is in a winding object state, and it is desirable to be referred to as 1-10nm. Furthermore, it is good to be



preferably referred to as 2-5nm.

[0064] It is desirable to equip the rechargeable battery of this invention with the PTC element whose induction temperature coefficient operation temperature is 140 degrees C - 80 degrees C, and is -10--130 as a safety device.

[0065] As a PTC element, it is BaTiO<sub>3</sub>. Although various things are known from the former, such as a ceramic system, the PTC elements which this invention defines are an overcurrent by conductive polymer with a PTC property (property that resistance becomes large as temperature goes up), and an overheat-protection element. For example, what is marketed from Raychem as protection elements various with the tradename of a Polyswitch (registered trademark) poly switch is mentioned. This element has the function which element resistance goes up automatically and intercepts current, when it sympathizes with both temperature and current and a fixed upper limit is exceeded. It is already well-known to equip a cell with this PTC element. For example, by equipping a lithium primary cell, when a cell short-circuits via an external circuit, this PTC element operates, current is intercepted, and practical use is already presented with securing the safety of a cell.

[0066] The following fact became clear as a result of this invention person's etc. examining the overcharge process of the rechargeable battery of this invention in detail.

[0067] \*\*. By the time it results in rupture at the time of overcharge, generation of heat should surely follow.

[0068] \*\*. The temperature rise of the cell by this generation of heat should be carrying out proportionality dependence at overcharge current.

[0069] \*\*. Correlate with overcharge current, and the cell can temperature surveyed at the time of rupture is so low that overcharge current is large, and the cell can temperature at the time of rupture is a bird clapper. (Since temperature rise speed is large, temperature distribution occur, and this is imagined to be what the low value is detected as rather than the temperature in an actual cell can.)

It is not more effective than the above fact to equip with the thermal fuse which responds only at temperature as a means to secure the safety at the time of overcharge of the rechargeable battery of this invention.

[0070] Moreover, when it equips with the current fuse which similarly responds only with current, the current precision which can respond is bad, distinction with normal current and overcharge current is impossible, and it is not the same effective means.

[0071] Therefore, the behavior at the time of overcharge of the rechargeable battery of this invention differs from the behavior of other cells greatly, and this is considered to be the behavior based on the combination of the active material of positive and negative two electrodes used with the rechargeable battery of this invention. therefore -- in order to secure the safety at the time of overcharge of the rechargeable battery of this invention -- both temperature and current - responding -- a value negative in the induction temperature coefficient -- it is -- in addition -- and it is required to have the induction temperature coefficient of the fixed range An induction temperature coefficient here is a parameter which is measured by the below-mentioned measuring method and shows the current dependency of induction temperature.

[0072] <Measurement of an induction temperature coefficient> A PTC element is connected to constant-current DC power supply, and the temperature up is carried out within oven, energizing fixed current (A). The temperature (degree C) at the time of the resistance of a PTC element increasing 1000 times at the time of a room temperature is measured. Current value is changed, the again same operation is performed, and a total of five points are measured. Temperature is plotted on a horizontal axis and the measured value of five points is plotted for current value on a vertical axis. Let this slope of a line be an induction temperature coefficient.

[0073] The operation temperature as used in the field of this invention means temperature in case resistance reaches 1000 times at the time of a room temperature only at temperature, when current value is zero.

[0074] The operation temperature of the PTC element used by this invention must be 80 degrees C - 140 degrees C. It is 85 degrees C - 140 degrees C preferably. In exceeding 140 degrees C, even if it compares and a PTC element operates at the temperature, generation of heat continues as it is, it results in rupture, the probability of the incorrect operation by practical use operating temperature limits becomes high at less than 80 degrees C, and it is not desirable.

[0075] Moreover, an induction temperature coefficient must be -10--130. desirable -15--100 -- it is -25--80 still more preferably

[0076] When an induction temperature coefficient is less than -ten, the case where the prevention to the surcharge in the large field of current value becomes less perfect, and explodes is generated. Moreover, in exceeding -130, the current value which can be energized a practical use field, i.e., near a room temperature, becomes small, and becomes practically unusable.

[0077] Although especially the method of equipping a cell with the PTC element of this invention is not limited, it is desirable for the method of equipping, for example in a cell can, the method of equipping a cell can free wheel plate, the method of equipping cell \*\*\*\*, etc. to be mentioned, and to equip the part which can detect the temperature of a cell to accuracy more with a natural thing.

[0078] By equipping with the PTC element which has the property of the above-mentioned range, the safety to a

surcharge is secured in all current ranges, and it is desirable.

[0079] In this invention, especially the moisture content in a cell can is important like the above. A moisture content here is a moisture content in the nonaqueous electrolyte in the state in the cell after assembly where it does not charge. For the following reason, this moisture is usually mixed.

[0080] Although especially the operation of the rechargeable battery of the moisture this invention which mixes in inside the moisture (c) . cell erector who contained in the cell member, such as a moisture (b) . positive electrode contained in (b) . nonaqueous electrolyte, a negative electrode, and a separator, by the atmosphere etc. is not limited The rechargeable battery of this invention has the high voltage of a single cell, since it can moreover obtain high-energy density, it is a single cell and the operation of making the pocket electronic equipment which consists of IC elements which operate by 3.5V-2.6V drive of it becomes possible. When the rechargeable battery of this invention is used by this operation, small lightweight-ization of pocket electronic equipment can be attained.

[0081] Being able to drive this pocket electronic equipment by 4.2V-2.5V, power consumption is about 3W-0.5W preferably below 4W. For example, there are a personal computer of 3.3V drive, an one apparatus video camera of 3.5V drive, a mobile transmitter of 3.3V drive, etc.

[0082] In this case, as a capacity of the rechargeable battery to be used, 400 or more mAhs, it is 1500 or more mAhs and 700 or more mAhs are 4000 or less mAhs still more preferably preferably.

[0083] In 400 or less mAhs, if prolonged continuous duty is not borne and 4000mAh(s) are exceeded, it will become difficult to achieve the purpose of lightweight-izing.

[0084]

[Example] Hereafter, an example explains this invention in more detail.

[0085] Example 1  $\text{Li}_{1.03}\text{Co}_{0.92}\text{Sn}_{0.02}\text{O}_2$  After mixing Li and the Co multiple-oxide 100 weight section which have composition, the graphite 2.5 weight section, and the acetylene black 2.5 weight section, the liquid made to dissolve the fluororubber 2 weight section in the 1:1 (weight ratio) partially-aromatic-solvent 60 weight section of ethyl acetate/ethylcellosolve was mixed, and slurry-like coating liquid was obtained.

[0086] The above-mentioned coating liquid was applied to both sides of with a width thickness [ 15micro thickness of 600mm ] aluminum foil using the coater which has a doctor blade coater head. The coating thickness after double-sided coating was 290micro.

[0087] The liquid made to dissolve the needle-coke trituration article 100 weight section and the fluororubber 5 weight section in the 1:1 (weight ratio) partially-aromatic-solvent 90 weight section of ethyl acetate/ethylcellosolve was mixed, and slurry-like coating liquid was obtained.

[0088] The above-mentioned coating liquid was applied to both sides of with a width thickness [ 10micro thickness of 600mm ] Cu foil using the coater which has a doctor blade coater head. The coating thickness after double-sided coating was 350micro.

[0089] Both did the slit of the two aforementioned kinds of coating articles to 41mm width after the press using the slit in the calendering roll.  $\text{Li}_{1.03}\text{Co}_{0.92}\text{Sn}_{0.02}\text{O}_2$  The coating article was made into the positive electrode, the needle-coke coating article was used as the negative electrode, and it wound with an outer diameter of 14.9mm in the shape of a coil with the winding machine, using the fine porous membrane (high pore 4030U Asahi Chemical Industry Co., Ltd. make) made from polyethylene as a separator. It is  $\text{LiBF}_4$  to the partially aromatic solvent of 1:1:2 (weight ratio) of propylene carbonate after putting this winding coil into a cell can with an outer diameter of 16mm / ethylene carbonate / gamma-butyrolactone. What was melted to 1 M concentration was obturated after sinking in as the electrolytic solution, and the cell can of A size with a height of 50mm shown in drawing 1 was made as an experiment.

[0090] In addition, - terms and conditions, such as a moisture content of the cell assembly atmosphere at that time and the electrolytic solution, were as being shown in Table 1.

[0091] It was 75 ppm, when this cell carried out after [ assembly ] opening and the moisture content of the electrolytic solution in a cell can was measured. The gas chromatograph (GC-14A, Shimadzu make) performed measurement of a moisture content. In addition, the column used the Porapak Q (1mx3phi).

[0092] When the cell assembled with the same lot was charged, there are also no phenomena, such as blistering of a cell can, and the normal cell performance was shown.

[0093] In examples 2-6 and one to example of comparison 2 example 1, except having made it the operating condition shown in Table 1, the completely same operation was performed and A size cell was made as an experiment.

[0094] Opening of the cell after each assembly was carried out, and the moisture content of the electrolytic solution in a can was surveyed. Moreover, the initial-charge examination was performed about each lot cell of this.

[0095] A result is combined and is shown in Table 1.

[0096]

[Table 1]

	電池組立 雰囲気	含浸に用 いた電解 液水分量	含浸前の 乾燥工程 の有無	電池缶内 の水分量	5サイクル目 の電流効率	電池缶の フクレの 有無
実施例 1	RH10 % の大気中	45ppm	有	75ppm	99.6 %	無
実施例 2	RH50 % の大気中	15ppm	有	18ppm	99.8 %	無
実施例 3	RH80 % の大気中	80ppm	有	135ppm	99.3 %	無
実施例 4	RH 1 % の大気中	10ppm	無	188ppm	99.5 %	無
実施例 5	RH 1 % の大気中	250ppm	有	298ppm	98.9 %	無
実施例 6	RH50 % の大気中	250ppm	有	320ppm	98.1 %	無
比較例 1	RH50 % の大気中	250ppm	無	650ppm	97.9 %	有
比較例 2	RH50 % の大気中	15ppm	無	480ppm	98.0 %	有

Except having performed the service condition of the coating machine when manufacturing the electrode sheet of a positive electrode and a negative electrode by the coating method in seven to example 12 example 1 on the conditions shown in Table 2, the completely same operation was performed and the trial production cell was created. The binder distribution factor of a positive electrode and a negative-electrode cell sheet obtained at this time was as being shown in Table 2.

[0097] The elevated-temperature cycle examination at 60 degrees C was performed about this trial production cell. The result is combined and is shown in Table 2.

[0098]

[Table 2]

	乾 燥 条 件		バインダー分布係数		60℃サイクル試験 100サイクル目の容 量 (%)
	正極	負極	正極	負極	
実施例 7	120℃熱風	120℃熱風	1.88	1.93	92
実施例 8	60℃熱風	遠赤外線乾燥	0.96	1.18	95
実施例 9	遠赤外線乾燥	120℃熱風	0.88	1.95	93
実施例 10	150℃熱風	遠赤外線乾燥	6.8	1.05	58
実施例 11	遠赤外線乾燥	150℃熱風	0.92	5.1	49
実施例 12	25℃風乾	25℃風乾	0.41	0.38	83

In 13 to example 16 example 7, except having used the copper foil which has surface roughness as shown in Table 3 as a negative-electrode charge collector, the completely same operation was performed and the trial production cell was created. The binder distribution factor of the negative-electrode electrode sheet obtained at this time was as being shown in Table 3.

[0099] The result of the capacity retention in 60-degree-C one-month retention test of the methanol immersing adhesive

property test of this negative-electrode electrode sheet and a trial production cell is also collectively shown in Table 3.

[0100]

[Table 3]

	銅箔 表面粗度	負極バインダー 分布係数	メタノール浸漬 接着性テスト	60℃1ヶ月保存後の 容量保持率
実施例 13	0.6 $\mu$	1.91	5分間までブリスター 発生せず。	89 %
実施例 14	0.3 $\mu$	1.95	〃	87 %
実施例 15	0.01 $\mu$	1.90	1分間までブリスター発 生せず。2分間でブリス ター発生。	61 %
実施例 16	0.04 $\mu$	1.91	〃	63 %

The completely same operation was performed except having used the slurry of the following composition as negative-electrode coating liquid in 17 to example 23 example 13.

[0101] The carboxymethyl-cellulose solution (1 % of the weight of solid contents) 100 weight section and the 1-/decanormal aqueous ammonia 1 weight section were added as the styrene / butadiene latex 10 weight section (50 % of the weight of solid contents) created by the composition shown in Table 4 to the needle-coke trituration object 100 weight section, and a thickener, and it mixed, and considered as coating liquid.

[0102] The result of the capacity retention in 60-degree-C one-month retention test of the methanol immersing adhesive property test of the negative-electrode electrode sheet obtained at this time and a trial production cell is also collectively shown in Table 4.

[0103]

[Table 4]

	ラテックスモノマー組成				ゲル含量 (%)	バインダー 分布係数	メタノール浸漬 接着性テスト	60℃1ヶ月保存 性の容量保持率
	ST	BD	MMA	IA				
実施例 17	47	40	10	3	83	1.75	5分間まで ブリスター発生せず	93 %
実施例 18	42	55	0	3	80	1.81	〃	92 %
実施例 19	33	60	5	2	98	1.95	〃	95 %
実施例 20	18	80	0	2	90	1.70	〃	94 %
実施例 21	4	95	0	1	78	1.51	〃	92 %
実施例 22	47	30	20	3	55	1.78	〃	88 %
実施例 23	0	100	0	0	80	1.79	2分間で ブリスター発生	73 %

ST : スチレン

BD : ブタジエン

MMA : メチルメタクリレート

IA : イタコン酸

各々重量%組成

[0104]

[Effect of the Invention] By making Li content multiple oxide into a positive active material, and setting to 5 ppm - 450 ppm the moisture content contained in the electrolytic solution in a cell can in the nonaqueous electrolyte cell which uses carbonaceous material for a negative-electrode active material, there is also no internal pressure elevation and cell properties, such as current efficiency, can be maintained so that clearly also from the above explanation.

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[Translation done.]